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X-ray Absorption Spectroscopy Studies of Model Catalysts

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Supported metal catalysts enable the production of essentially all forms of liquid hydrocarbon fuels as well as facilitate a multitude of other industrial processes. Catalytic behavior is influenced by a plethora of competing factors of which the most important is catalyst structure. The catalyst size, on which structure is strongly reliant, complicates its study by pushing the limitations of qualitative and quantitative analyses. In general, it can be said that 30 nm marks a transition into improved catalytic ability and, in some cases, the onset of dramatically distinct behaviors in small clusters [1]. It therefore remains a significant goal in science to fundamentally understand and predict the local structure and stability of catalytic materials at this scale so that tailor-made catalysts with distinct technological applications can be created. Dramatic progress toward this idea of “rational catalyst design” through the combined use of simulation and experimentation is already being realized by several groups [2–5].

We focus here on the development of X-ray absorption spectroscopy (XAS) data modeling tools and their applications appropriate for carrying out detailed studies on nanoscale metallic clusters. The X-ray absorption near edge structure (XANES) region of XAS allows investigators to monitor the oxidation state and perturbations to the electronic structure of a sample. The extended X-ray absorption fine structure (EXAFS) exhibits excellent spatial resolution and is, consequently, one of the premiere techniques used to probe the local atomic environment of small particles [6]. When these techniques are combined it becomes possible to simultaneously describe both the geometric and the electronic aspects of nanoparticles that are so crucial to catalytic performance.

Despite the extreme sensitivity of XAS, it remains a bulk technique and requires that samples possess a narrow size distribution if meaningful results are to be obtained. Toward this end, electron microscopy is often employed as a complementary technique because of its ability to quantitatively determine the size distribution within a sample. Consequently, XAS can then be applied on verified model systems chosen for their ability to provide important fundamental understandings of the atomic and electronic structure of catalysts. Elucidation of such information enables critical insights into the complex systems found in real catalytic processes.

Following the flow of charge

It is now widely appreciated that very small metal clusters exhibit improved patterns of catalytic activity compared to their respective bulk states [7, 8]. Perhaps the most important example of this is found for Pt nanoparticles supported on γ - Al_2O_3 , which is the system of choice for refining petroleum products [9]. This demanding process has been found to proceed more economically as the size of the catalyst decreases. Thus, thorough characterization of such a prototypical catalyst is of profound interest. The atomic structure of this particular system was investigated in a past EXAFS experiment through the examination of nanoparticles that were only ca. 0.9 nm in diameter. Analysis of the resulting spectra revealed that the supported Pt nanoparticles displayed anomalous behavior, featuring negative thermal expansion (NTE) and large static disorder in average atomic positions. XANES measurements of these samples also showed perturbations in the white line intensity and edge energy – features consistent with changes in the electronic charge state of the clusters [10, 11].

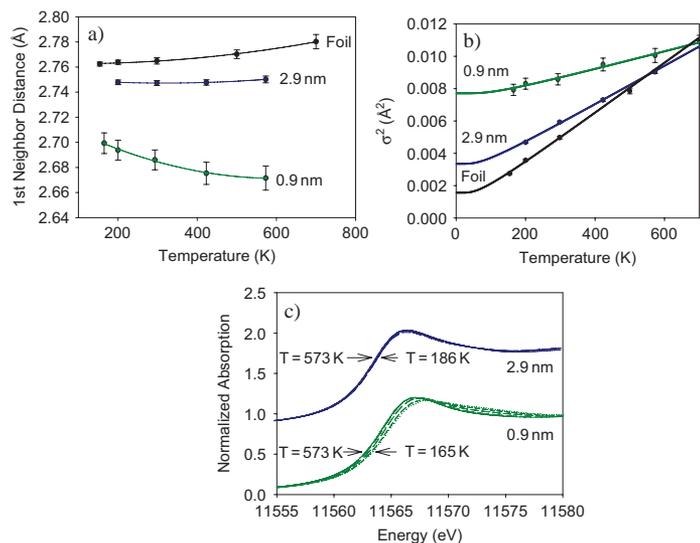


Figure 1: Temperature dependence of the Pt/ γ - Al_2O_3 samples under an He atmosphere with respect to the measured: (a) 1NN Pt-Pt bond length; (b) 1NN Pt-Pt bond length's mean square disorder; and (c) XANES region showing an increasing edge shift – indicates the presence of charge transfer – with decreasing particle size.

More recently, EXAFS experiments conducted on slightly larger (1 nm and 3 nm) Pt nanoparticles supported on γ -Al₂O₃ and subjected to similar conditions as the aforementioned study (i.e., temperature ramps under inert and reactive gas-phase atmospheres) also revealed these anomalous behaviors (Figure 1 a and 1b). Probing the electronic structures of the particles with XANES showed the sensitivity of the charge-transfer magnitudes to the cluster sizes (Figure 1c). It was further discovered that XANES showed a remarkable sensitivity and exhibited characteristic trends corresponding to specific adsorbate and support interactions. These results were explained self-consistently by theoretical XAS studies conducted by Vila et al. [12]. Collectively, these experiments illustrate a complex behavior with competing interactions where the anomalous effects in thermal and electronic properties are driven by large dynamic fluctuations of the cluster-support system. The information obtained offered new insight into the electronic and atomic structure as well as the structural dynamics of an immensely important catalytic system [12–15].

Revealing the shape and coordination of nanoparticle systems

Gold, conventionally an inert (noble) material, begins to exhibit catalytic behavior as it approaches nanoscale dimensions. When placed on a support, Au nanoparticles have found use as catalysts for the selective oxidation of hydrocarbons and the oxidation of carbon monoxide [16–19]. Industrially, the former conversion represents a very demanding two-step reaction but is found to proceed through a facile, one-step mechanism when very small (~2–3 nm) supported Au clusters are used. The latter example presents a reaction that can be used toward the remediation of automotive exhaust; specifically, conversion of toxic CO to a more harmless species (CO₂) [16, 20]. Insight into the specific geometric forms that contribute to dissimilarities in catalytic activity can be obtained using XAS.

As mentioned, model clusters with an exceptionally narrow size distribution can allow one to discern an applicable atomic packing structure (e.g., closed packed vs. non-closed packed) [21]. To demonstrate EXAFS sensitivity to cluster geometry, we consider mixed-ligand stabilized Au clusters containing an average of 13 atoms [22]. These structures were shown to possess icosahedral packing whereas larger, thiolate-stabilized Au clusters were found to possess a face-centered cubic (fcc) structure. In both cases, EXAFS analysis yielded information in real-space distances (r-range) well beyond the first nearest neighbor distance (Figure 2). For clusters of this size, an icosahedral geometry would contain no linkages corresponding to the second nearest neighbors pair in an fcc cluster as Figure 3 demonstrates. Thus, if no peak is observed in the corresponding r-region in the Fourier transform of the 13-atom clusters, one can conclude that the clusters' structures are inconsistent with an fcc packing — as we have shown in Ref. 21. For larger, thiolate stabilized clusters, we detected a prominent peak in the r-range, signaling the existence of a closed-packed structure.

Additional information about the ligated Au system was obtained by analyzing the coordination number and bond distances of Au-S and

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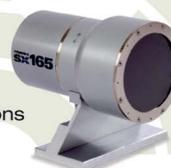
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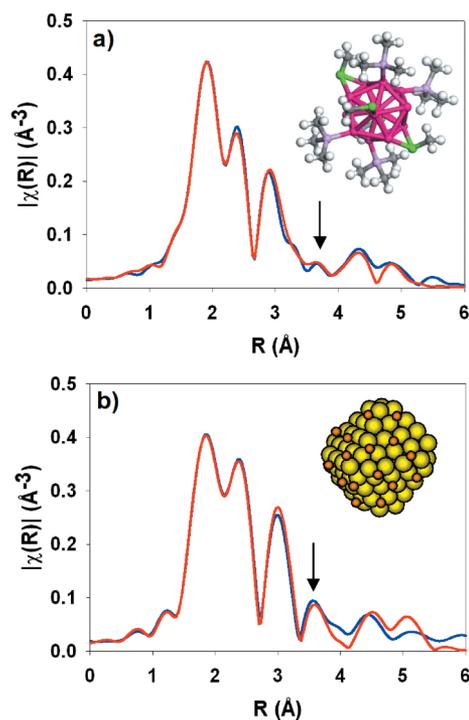


Figure 2: Fourier transform magnitudes of the K^3 -weighted EXAFS data (blue) and theoretical fit (red) for: (a) $Au_{13}(PPb_3)_4(SC_{12})_4$; and (b) fully thiolated clusters. The insets show proposed structures for the Au_{13} clusters and an Au_{140} cluster that represents the average size of the fully thiolated MPCs. The arrows indicate a region in which a peak would be indicative of an fcc structure.

Au-P obtained by EXAFS. The data obtained was then used to propose possible binding configurations for the attached ligands. Using this information it was possible to construct a final structure where Au-S bonds occurred at both on-top and bridge-top sites while all Au-P bonds were limited to bridge-top sites. This structure was in excellent agreement with that obtained using first principle calculations [23]. Therefore, EXAFS analysis can be utilized to determine discrete structural features found in a material. Such clarification of a system's packing structure is crucial for catalysts, such as Au nanoparticles, where slight structural modifications can result in a biased chemical pathway [24].

Probing the structure of bimetallic nanoparticles

We now turn to bimetallic alloys, a second type of catalytic system of tremendous interest to catalysis science because of numerous instances where increased catalytic activity and resistance to poisoning arise from the introduction of a secondary metal. By using a multiple-edge data analysis scheme and applying physically reasonable constraints, one can discriminate between different structural models for

the bimetallic nanoclusters. For instance, using the EXAFS-derived coordination numbers and elemental composition, the relative apportionment of the comprising elements within the bimetallic catalyst can be determined (e.g. core-shell, random alloy) [21].

This EXAFS analysis is well illustrated by an experiment in which the morphological change of dendrimer-protected Pd/Au nanoparticles is monitored before and after the removal of the protective dendrimer. Preliminary EXAFS of these electrochemically active catalysts revealed that the encapsulated clusters were comprised of a quasi-random alloy that exhibited a surface enrichment of Pd irrespective of the initial ratio of the precursor metals. Upon removal of these particles from their dendrimer hosts, the particles experienced a structural rearrangement in the form of phase segregation. The results indicated that after extraction the bimetallic nanoparticles adopted a structure consistent with that of Au/Pd core-shell particles [25]. The real space data of the random alloy samples at the Pd edge contained two scattering centers, representing the Pd-Pd scattering contribution and Pd-Au contributions. Upon removal of the dendrimer, the Pd edge data showed one scattering contribution attributed to Pd-Pd bonding, indicating a Pd-rich phase having minimal contact with Au. Quantitative analysis of the data indicated that coordination of Pd-Au decreased while Pd-Pd coordination increased, coincident with dendrimer removal and consistent with trends predicted for the formation of a core-shell structure.

While studying the transition between a bimetallic alloy and a phase segregated system is an area where EXAFS serves as a particularly useful characterization tool, the interaction of nanoalloys with their environment (adsorbates and/or support) is seen as an even higher level of complexity, capable of being probed by EXAFS/XANES. The response to external stimuli becomes particularly important if the area where the catalyst is to be employed will only experience moderate environmental control. A representative example is polymer electrolyte

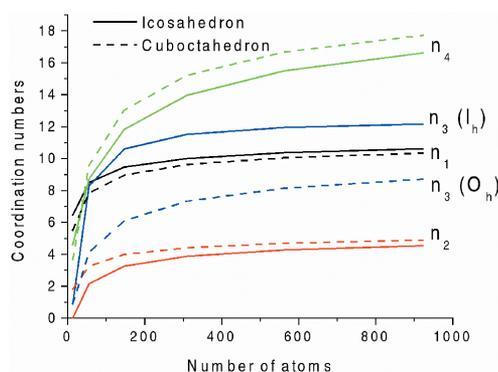
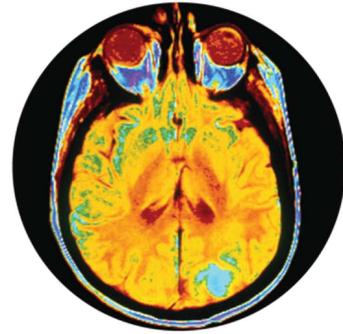
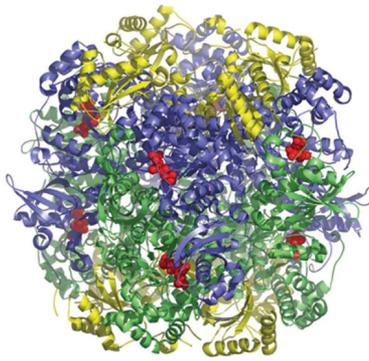


Figure 3: Calculated nearest neighbor coordination numbers for the first three shells of ideal cuboctahedral and icosahedral clusters.



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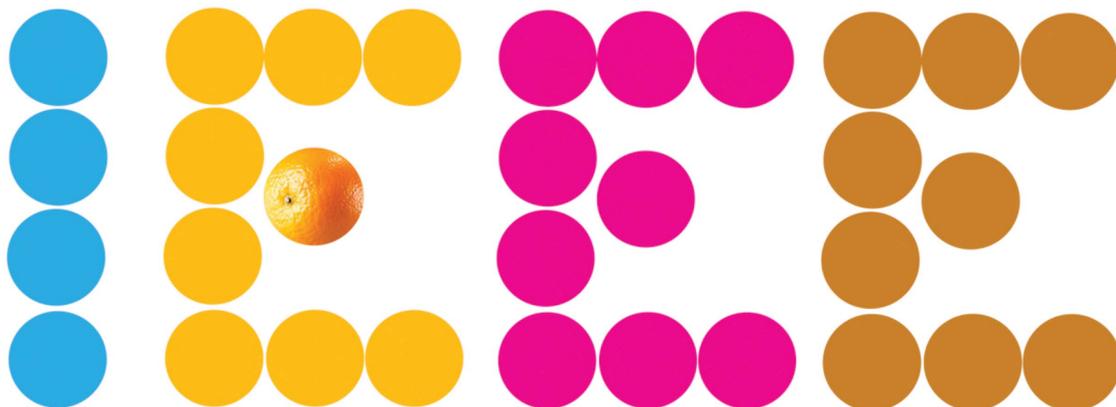
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membranes (PEMs) using Pt/Ru nanoparticles in direct oxidation fuel cells [26–28]. The carbon supported Pt/Ru particles examined by Nashner, et al. serve to illustrate how intricate the interactions of these particles and their environment can be. EXAFS characterization of the sample showed that the clusters adopted a Pt-core/Ru-shell structure upon their synthesis from molecular cluster precursors [29]. However, upon reduction with hydrogen at an elevated temperature, distinct and reversible structural changes in which Pt segregated to the surface of the clusters occurred. Of particular interest are the markedly non-bulk behaviors of Pt and Ru atoms within the nanoalloy revealed by EXAFS. The bulk packing structure of Ru is hexagonal close-packed (hcp), whereas bulk Pt possesses an fcc structure. As previously mentioned, it is possible to use EXAFS to discern which packing structure(s) are present in a monodisperse sample. Applying this analysis to the Pt/Ru sample uncovered the surprising result that, instead of reverting to its bulk-like hcp packing, Ru actually adopted an fcc packing upon its migration into the particle core – essentially using the original (Pt) core's packing as a template for the final particle structure [29].

This is not the only instance of one crystal structure effecting the final shape of a nanoparticle. Molenbroek et al. examined an Ni/Au nanoparticle system for use in the steam reforming process. Using quick EXAFS (QEXAFS) technique in conjunction with mass spectroscopy, the authors were able to follow the reaction under realistic conditions. The data showed that although the reaction initially proceeded at a slower rate versus a pure Ni catalyst, its activity remained unchanged long after the Ni catalyst had been deactivated by carbon deposition. Using Monte Carlo simulations the authors found that the Au atoms were preferentially located on the kink and edge sites (i.e., most reactive sites) of the Ni nanoparticle in which they were alloyed. This was offered as evidence that Au alloying prevents deactivation of the Ni catalyst by occupying highly reactive sites where carbon whiskers might form through the adsorption of carbon [30].

Iridium is another metal that is typically added to Pt catalysts, primarily because of its protective properties against poisoning [31, 32]. Recent EXAFS and XANES analysis of bimetallic Pt/Ir nanoparticles supported on γ - Al_2O_3 focused on examining the thermal, structural and electronic

properties of both the Pt and Ir L_3 edges under different atmospheric conditions (H_2 and He) [33]. Much like the experiments of Pt/ γ - Al_2O_3 discussed here, the Pt/Ir system revealed similar elements of complexity (mobility, cluster-support and cluster-adsorbate interactions). Additionally, the particles were found to feature metal-metal interactions within the clusters in the form of charge transfer between Ir and Pt atoms (Figure 4). In this respect, XANES allowed for useful monitoring of the changes to electronic structure in the two metals. Further treatment of the results could help explain the resiliency of Pt/Ir catalysts to poisoning in comparison to their monometallic counterparts.

Looking toward the future

The development of more efficient catalysts is contingent on a methodical method of construction. And, like any other form of construction, deliberate catalyst engineering requires both a blueprint for the structure and an understanding of how the materials being used will behave. We have attempted to demonstrate that, by studying model systems, it is possible to obtain information highly relevant toward the synthesis of new catalysts that possess unique structural and electronic properties. Theoretical XAS studies have managed to successfully reproduce real XAS experiments and, thus, identify the most probable sources of structural and dynamic trends associated with real catalytic systems [12]. Additionally, electron microscopy has confirmed the sensitive nature of XAS measurements when applied to monodisperse samples. To this effect, current advances in electron microscopy have shown the potential for atomic resolution. This could bridge the gap between structure and function, allowing for direct verification of atomic structure and, with the help of XAS, a 3-D reconstruction of the prototypical catalyst.

In conclusion, using XAS in conjunction with other analytical techniques offers sorely needed illumination of the as-yet poorly understood link between the function of a catalyst and factors such as the size, shape, support, adsorbates, and heterogeneity on a much larger scale. Ultimately, these properties may be tailored such that a type of dynamic nanoparticle catalyst, one capable of selectively catalyzing different reactions based on some external stimulus, can be created.

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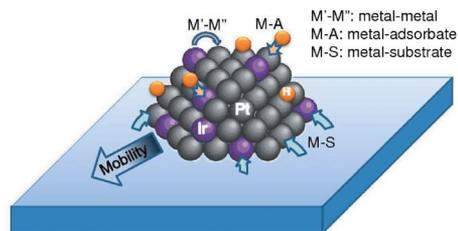


Figure 4: Schematic of the competing interactions in supported bimetallic catalysts, shown in an [IrPt]/ γ - Al_2O_3 system.

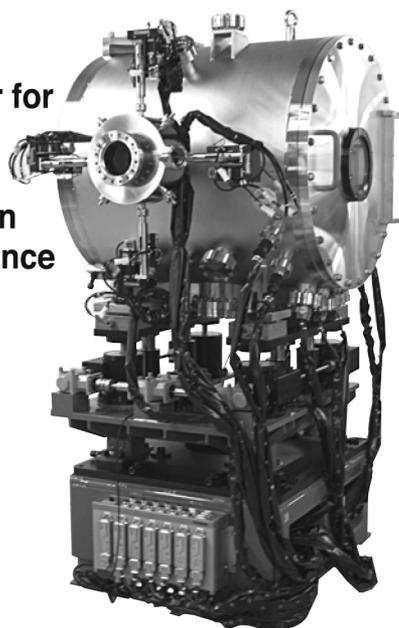
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